

QUANTITATIVE GAS ANALYSIS BY MASS SPECTROMETER
(No. 3) — QUANTITATIVE ANALYSIS OF CARBON
MONOXIDE AND NITROGEN

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Mitsuo Hayakawa

ABSTRACT. The problem of separating compounds with similar M/e using a mass spectrometer is discussed. One possible solution is to oxidize one of the components by chemical means. A method using copper oxide is described.

Introduction

Analysis by a mass spectrometer is generally called mass analysis. Although the method has many advantages as previously reported [1, 2], it also has disadvantages, and can cause relatively great errors in the following cases:

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(1) Analysis of mixtures that contain polar substances.

(2) Analysis of mixtures that contain more than two components having similar masses.

The error caused by (1) arises from the relatively strong attraction of polar substances on the instrument wall. The shortcoming, however, is now being overcome by the technique devised by Brown and Washburn [3, 4, 5]. The error from (2) results from the basis of the mass spectrometric analysis; ions that have similar M/e (M is a mass measured relative to the

* Numbers in the margin indicate pagination in the original foreign text.

mass of hydrogen, e is the number of charges) occupy the same position in the mass spectrum. Organic compounds normally produce a corresponding quantity of fragment ions to the parent ion. Since the probability of ionization of the fragment ions is large compared to that of the parent ion, the error can be generally neglected. Therefore, the only time the error caused by (2) becomes important is when the ionization probability of the fragment ions is small compared to that of the parent ion. Such an example is the analysis of a gas mixture that contains carbon monoxide and nitrogen. This does not infer that mass analysis of such gas mixtures is impossible. The amount of N_2 ions can be calculated from the amount of N^+ , and the amount of CO^+ can be calculated from the amount of C^+ . The error, however, is relatively large for the reasons given above.

In order to overcome such shortcomings, either a larger magnet can be employed to enhance the separation of ions, or the energy of the collision electronic current can be increased to improve the ionization probability. However, since the difference in the masses of N_2 and CO is small, the increase in the energy of electron collision current does not necessarily enhance the ionization probability to the desired extent. Such methods complicate the instrumentation, and reduce the advantages of mass spectrometric analysis. The alternative is to oxidize only CO by chemical means to effect the separation from N_2 . In this report, a quantitative separation method using copper oxide is presented as an attempt to effect such a separation. /753

Experimental Part and Results

The mass spectrometer used in this experiment is a 90° convergent type — details can be found in the previous report [6]. Three types of gas mixtures used as samples were obtained

from an electrical furnace from the melting of casting materials, and contain N_2 , CO , O_2 , and CO_2 .

The main portion of the experimental set-up is shown in Figure 1. F is an electrical furnace which is heated to $270^\circ C$ and is filled with combustion tubes whose inner diameter and length are 4 mm and 40 cm, respectively. The combustion tubes contain cylindrical copper oxides for the elemental analysis. The volume of gas cylinder R is approximately 11 l. The volumes of ABC and AFD sections are approximately the same (30 cc), and can be neglected compared to that of the gas cylinder R. The volume of the auxiliary gas cylinder R' is approximately 200 cc.

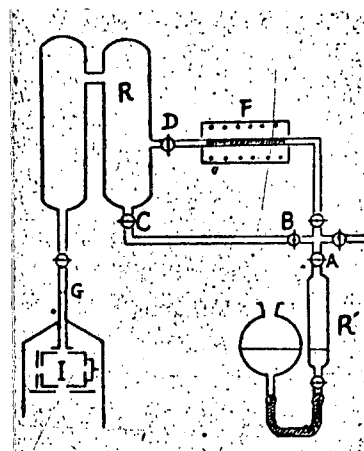


Figure 1

After the whole system is thoroughly evacuated, the auxiliary gas cylinder R' is filled with the sample gas to a constant pressure in the range of $3 \sim 6 \times 10^{-1}$ mm Hg (so that the pressure becomes $1 \times 10^{-2} \sim 5 \times 10^{-3}$ mm Hg when it is introduced into R). It is then introduced into R via ABC and fed into the mass spectrometer through the gas supply G. From the above measurements (1), the mole ratios of H_2 , O_2 , and CO_2 in the ionization chamber (I) and, therefore, their volume ratios in the gas cylinder R can be determined. Subsequently, the system is again thoroughly evacuated, and the auxiliary gas cylinder R' is filled with the sample gas to the same pressure P as in measurement (1). It is then introduced into R through the electrical furnace F, and the mass spectrum is taken as in measurement (1). From the results of this measurement (2) and

the previous measurement (1), the volume ratio of N_2 and CO in R can be determined. Assuming complete oxidation of CO by the copper oxide, and if the adsorption of each gas component can be neglected, a quantitative analysis of the sample gas can be made according to the theory described in Table 1.

TABLE 1. COMPUTATION THEORY
Measurement (1)

Components	Gas cylinder (R)		Ionization chamber	
	No. of moles	Partial pressure	No. of moles	Peak height
H_2	a	$k \cdot a$	$k' \cdot a$	$(I_2)_1$
O_2	b	$k \cdot b$	$k' \cdot b$	$(I_{22})_1$
CO_2	c	$k \cdot c$	$k' \cdot c$	$(I_{44})_1, (I_{22})_1$
N_2	d	$k \cdot d$	$k' \cdot d$	$(I_{22})_1$
CO	e	$k \cdot e$	$k' \cdot e$	$(I_{22})_1$

$$k' \cdot a = (I_2)_1 / \eta_{H_2}, k' \cdot b = (I_{22})_1 / \eta_{O_2}, k' \cdot c = (I_{44})_1 / \eta_{CO_2}$$

$$\Sigma (I_{22})_1 = k' \cdot c \cdot \eta_{CO_2 \rightarrow CO} + k' \cdot d \cdot \eta_{N_2} + k' \cdot e \cdot \eta_{CO}$$

Measurement (2)

Components	Gas cylinder (R)		Ionization chamber	
	No. of moles	Partial pressure	No. of moles	Peak height
H_2O	$a' (\approx a)$	$k \cdot a'$	$k' \cdot a'$	$(I_{12})_2$
O_2	$b' (\approx b)$	$k \cdot b'$	$k' \cdot b'$	$(I_{22})_2$
CO_2	$c+e$	$k(c+e)$	$k'(c+e)$	$(I_{44})_2, (I_{22})_2$
N_2	d	$k \cdot d$	$k' \cdot d$	$(I_{22})_2$

$$(I_{44})_2 = k'(c+e) \cdot \eta_{CO_2}$$

$$\Sigma (I_{22})_2 = k' \cdot d \cdot \eta_{N_2} + k'(c+e) \cdot \eta_{CO_2 \rightarrow CO}$$

From measurements (1) and (2), we have

$$k' \cdot c = \frac{1}{\eta_{\text{CO}_2^+}} \{ (I_{44})_2 - (I_{44})_1 \}$$

$$k' \cdot d = \frac{1}{\eta_{\text{N}_2^+}} \{ \sum (I_{28})_2 - k'(c+e) \cdot \eta_{\text{CO}_2 \rightarrow \text{CO}^+} \}$$

The main ions are listed in the peak height column in Table 1. $(I_x)_1$ is the ionic weight $M/e = x$ from measurement (1). η_i is the ionization probability, that is, $\eta_{\text{CO}_2^+}$ and $\eta_{\text{CO}_2 \rightarrow \text{CO}^+}$ are the ionization probabilities of CO_2^+ from CO_2 and CO^+ from CO_2 , respectively. The same is true for the others. The measured values in the previous report [7] are used for the calculations.

Figure 2 summarizes the experiment that was conducted to insure that the oxidation of CO by the copper oxide heated to 270° C is complete, and that the adsorption of CO and CO_2 by the oxide is negligible. \circ and \bullet are the measured values of pure CO_2 , and Δ and \blacktriangle are those of pure CO oxidized by the combustion tubes F in Figure 1. The solid line in Figure 2 indicates CO_2^+ from CO_2 , and the dotted line represents dissociated ions CO^+ from CO_2 .

The analytical results on the three types of sample obtained from the computation theory shown in Table 1 are summarized in Table 2.

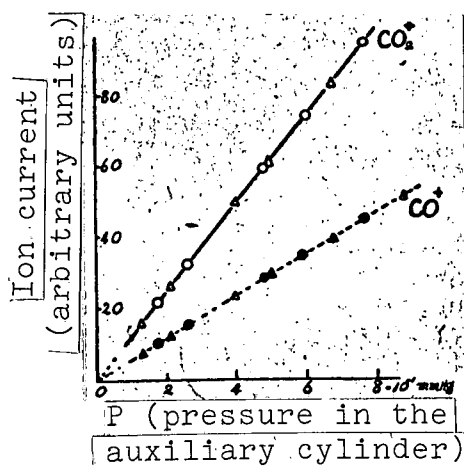


Figure 2

Reference was made to the measured values of Tate [8] for the computation of NO. The chemical analysis in Table 2 was done by the absorption method. The Palladium method was used for the analysis of H₂.

Experimental Results and Discussion

The method requires that CO be completely oxidized by copper oxide, and also that the adsorption of gases on copper oxide is negligible at 270° C. The results shown in Figure 2

TABLE 2

Sample	Composition	Quantitative analysis (vol %)	Chemical gas analysis (vol %)
A	H ₂	1.90	1.7
	O ₂	0.90	0.7
	CO	73.50	72.6
	CO ₂	1.26	1.5
	N ₂	22.73	23.5
	NO	0.31	
B	H ₂	9.60	2.7
	O ₂	6.14	5.4
	CO	56.87	56.1
	CO ₂	5.43	6.5
	N ₂	27.48	29.3
	NO	0.48	
C	H ₂	3.10	3.4
	O ₂	6.16	5.4
	CO	50.33	49.2
	CO ₂	10.22	9.6
	N ₂	29.65	32.4
	NO	0.54	

and Table 2 show that these requirements are fulfilled. Therefore, satisfactory results were obtained by the quantitative separation method. Although the computation may become complicated, the method is applicable to the quantitative analysis of mixtures which contain hydrocarbons (ethylene, etc.) in addition to CO and N₂.

A problem arises, however, when one of the components — CO or N₂ — is present in minute amounts (for example, ~ ppm) because its adsorption on copper oxide is not negligible. In this case, the error becomes relatively large (with respect to the minute fraction). Improvements in the analysis of such special gas mixtures remain to be made.

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